

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

In re Application of:  
Jim Butler et al.  
Serial No.: 10/749,259

Confirmation No.: 8566

Filed: December 31, 2003

**For: USING EXCESS LEVELS OF  
METAL SALTS TO IMPROVE  
PROPERTIES WHEN  
INCORPORATING POLYMERS  
IN ASPHALT**

§ Examiner: Peter Mulcahy

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Group Art Unit: 1713

Attorney Docket No. COS-890

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Dear Honorable Commissioner:

<p><b>CERTIFICATE OF TRANSMISSION</b></p> <p>I hereby certify that this correspondence is being facsimile transmitted to the United States Patent and Trademark Office to the Board of Patent Appeals and Interferences to fax number 571-273-0053 on:</p> <p>Date: <u>March 13, 2007</u></p> <p>Signed: <u>[Signature]</u> Typed or printed name of signing certificate</p>
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**FIRST SUPPLEMENT TO APPEAL BRIEF**

Appellants submit this First Supplement to the Appeal Brief filed December 22, 2006, to the Board of Patent Appeals and Interferences on appeal from the decision of the Examiner of Group Art Unit 1713 dated June 28, 2006, finally rejecting Claims 1-3, 5-11, 12-20, 23-24, 26, 28, 30-32, 35-37, 39-47, and 49-50.

In response to the Notice of Non-Compliant Appeal Brief dated 13 February 2007, and in response to the Advisory Action After the Filing of an Appeal Brief dated 24 January 2007, please substitute and replace the following sections of the originally filed Appeal Brief with the sections set forth below.

***Appendix A***, of Pending Claims also is attached hereto.

The Supplement to the Appeal Brief is not submitted in triplicate because it was transmitted by facsimile and is voluminous.

**Status of Claims**

The claims pending in the application at the time of the final rejection and the filing of the Notice of Appeal were Claims 1-3, 5-11, 12-20, 23-24, 26, 28, 30-32, 35-37, 39-47, and 49-50.

The Examiner entered an Amendment under 37 CFR 1.116 that was filed with the original Appeal Brief, on 24 January 2007. Thus upon entry of that amendment under 37 CFR §1.116, Claims 1-3, 6-11, 12-20, 23-24, 26, 28, 30-32, 35-37, 39-47, and 49-50 are pending for consideration on appeal. Those pending claims were previously shown in *Appendix A*, which was attached to the original Appeal Brief.

### **Status of Amendments**

An Amendment under 37 CFR 1.111, was sent by facsimile on April 11, 2006. It was followed by a final rejection. Subsequently an Amendment after final under 37 CFR 1.116, was sent by facsimile on August 25, 2006. However the Amendment was not entered because according to the Advisory Action of September 8, 2006, it raised new issues that would require further consideration and/or search and such amendment was not deemed to place the application in better form for appeal.

The Examiner has entered an Amendment under 37 CFR 1.116 that was currently filed with the original Appeal Brief. In that amendment, Claim 1 was rewritten to incorporate the subject matter of Claim 5, and two simple typographical errors were corrected.

### **Summary of Claimed Subject Matter**

The invention described by the claims on appeal involves asphalt *compositions* (*Independent Claims 26, 43, and 49*) and *methods* (*Independent Claims 1, 17, 23*) for preparing asphalt compositions, along with methods for road paving (Claim 15), a paved road (Claim 41) and methods for sealing of a roof with such asphalt compositions (Claim 16) as well as a sealed roof (Claim 42).

In one aspect of the invention, the *method* for preparing asphalt and polymer includes: heating (Par. 0039 of Published Application) a mixture of asphalt (Par. 0023) and an elastomeric polymer (Par. 0024), adding from about 0.05 weight % (wt%) up to 5 weight % (wt%) of a metal salt (Pars. 0041, 0042), based on the weight of the asphalt/polymer mixture. Independent Claim 1. In an aspect, the metal of the metal salt is chosen from zinc, cadmium, mercury, copper, silver, nickel, platinum, iron, magnesium, and mixtures thereof. Claim 1; Par. 0041. Where the metal salt is a metal oxide, it is chosen from zinc oxide, calcium oxide and combinations thereof. Claim 3; Par. 0041. In an aspect, the compatibility of the asphalt and polymer composition prepared with the metal salt amount is improved as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal salt amount. Independent Claim 1; Pars. 0021, 0041. A crosslinker may also be added to the asphalt mixture (Claim 6; Par. 0029), and includes elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof (Claim 7, Par. 0029); 0.01 to 0.4 wt% of the crosslinker is added, based on the weight of the asphalt/polymer mixture (Claim 9, Par. 0029). In one aspect, the metal salt proportion is at least about five times greater than the crosslinker proportion. Claim 47; Par. 0042. Further, ground tire rubber (GTR) may also be added to the mixture of asphalt (Claim 35; Pars. 0044-0046) and ranges from about 1 to about 20 wt% of the mixture. Claim 50; Pars. 0044, 0046. It has been found that the GTR and mixture of asphalt and an elastomeric polymer (Claims 11, 36; Par. 0020) is more homogeneous as compared to an identical mixture of GTR, asphalt and elastomeric polymer where a lesser amount of metal salt is used. Claims 13, 39; Pars. 0020, 0021.

As a further advantage, the asphalt and polymer compositions prepared with the metal salt amount have reduced gels as compared with the identical asphalt and polymer composition having a lesser metal salt amount. Claims 14, 40; Pars. 0021, 0029).

In an alternative embodiment, the *method* for preparing asphalt and polymer compositions includes: heating a mixture of asphalt and an elastomeric polymer, adding from about 0.05 wt% up to 5 wt % of a metal oxide such as zinc oxide, iron oxide, copper oxide, magnesium oxide, calcium oxide, and combinations thereof, where the compatibility of the asphalt and polymer composition is improved as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal oxide amount. Claim 17; Pars. 0023, 0024, 0039, 0041-0042. In one aspect, a crosslinker (Claim 19; Par. 0029) such as elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof is also added to the mixture (Claim 20; Par. 0029).

In another embodiment the *method* for preparing asphalt and polymer compositions includes: heating a mixture of asphalt and an elastomeric polymer, adding from about 0.05 wt% up to 5 wt% of a metal oxide, where the metal of the metal oxide is selected from Groups IIA and IIB of the Periodic Table (CAS notation) Pars. 0017, 0020, 0041, adding ground tire rubber (GTR) to the mixture of asphalt and elastomeric polymer before or after the metal oxide is added, where the GTR and mixture of asphalt and elastomeric polymer is more homogeneous as compared to an identical mixture of GTR, asphalt and elastomeric polymer having a lesser amount of metal oxide. Claim 23; Pars. 0023, 0024, 0039, 0041-0042. In an aspect, from about 1 to about 20 wt% of the GTR is added. Claim 24; Par. 0041.

The invented *asphalt composition* includes: asphalt, an elastomeric polymer, and an organic or inorganic metal salt present in an amount from about 0.05 wt% up to 5 wt% based on the weight of the asphalt/polymer mixture; the metal portion of the salt can be zinc, cadmium, mercury, copper, silver, nickel, platinum, iron, magnesium, and mixtures thereof. Claim 26; Pars. 0018, 0023, 0024, 0041-0042. In an aspect of the invention, the metal salt is zinc oxide, calcium oxide, and combinations thereof. Claim 28; Par. 0041. The compatibility of the polymer modified asphalt (PMA) is improved as compared with the compatibility of an identical PMA having a lesser metal salt amount. Claim 30; Pars.

0021, 0041. In one aspect, a crosslinker chosen from elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof are added to the PMA. Claim 32; Par. 0029. Also, ground tire rubber (GTR) can also be added to the asphalt (Claim 35) in an amount of from about 1 to about 20 wt% of the PMA. Claim 36; Par. 0041. A mixture of GTR and PMA is more homogeneous with 0.05 wt% up to 5 wt% of the metal salt as compared to an identical mixture of GTR and PMA having a lesser amount of metal salt. Claim 39; Pars. 0020, 0021, 0044. In an aspect, a road is made from the PMA and aggregate. Claim 41; Pars. 0010, 0023. In another aspect, a roof is sealed with the PMA. Claim 42; Par. 0010.

In another aspect, the invented asphalt *composition* includes: asphalt, an elastomeric polymer, and a metal oxide chosen from zinc oxide, calcium oxide and combinations thereof, in an amount at least from about 0.05 wt% up to 5 wt% based on the weight of the asphalt/polymer mixture, where the compatibility of the asphalt and polymer composition is improved as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal oxide amount. Independent Claim 43; Pars. 0022, 0024, 0041, 0042. In an aspect, the metal oxide is zinc oxide in an amount of from 0.05 to about 2 wt.% based on the combined amount of asphalt and elastomeric polymer. Claim 44; Par. 0042. In a further aspect, the PMA also includes a crosslinker. Claim 45; Par. 0042. In an aspect, the crosslinker is chosen from elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof. Claim 46; Par. 0029. In a further aspect, the metal oxide proportion is at least about five times greater than the crosslinker proportion. Claim 47; Par. 0042.

In a further aspect, the asphalt *composition* includes: asphalt, ground tire rubber (an elastomeric polymer), and metal oxide in an amount at least 0.05 wt% up to 5 wt% based on the weight of the asphalt/polymer mixture, where the metal of the metal oxide is selected from Groups IIA and IIB of the Periodic Table (CAS notation), and where the asphalt composition is more homogeneous than an identical mixture of GTR, asphalt, and elastomeric polymer having a lesser amount of metal oxide. Claim 49; Pars. 0017, 0020, 0041. In an aspect, the GTR ranges from about 1 to about 20 wt% of the mixture. Claim 50; Par. 0041.

A method of road building is also contemplated and includes adding aggregate to the invented asphalt composition and forming a road paving material, then using the material to form road pavement. Claim 15; Pars. 0010, 0023.

A method of sealing a roof is also contemplated and includes heating the asphalt composition and distributing it over at least a portion of a roof surface. Claim 16; Par. 0010.

Experimental Examples of the asphalts of this invention and the methods of making such asphalts are set forth in Pars. 0049-0086 and Tables I-VII.

**Grounds of Rejection to be Reviewed on Appeal**

The prior art that was relied upon in rejecting the claims is limited to U.S. Patent No. 6,713,539 to *Guo et al.* The grounds of rejection to be reviewed on appeal is whether the Examiner erred in rejecting Claims 1-3, 5-11, 12-20, 23-24, 26, 28, 30-32, 35-37, 39-47, and 49-50 under 35 U.S.C. §103(a) as being unpatentable over *Guo et al.*, U.S. Patent No. 6,713,539.

In the arguments presented in this Brief, all of the claims do not stand or fall together.



### Argument

**THE EXAMINER ERRED IN REJECTING CLAIMS 1-3, 5-11, 12-20, 23-24, 26, 28, 30-32, 35-37, 39-47, AND 49-50 UNDER 35 U.S.C. §103(A) AS BEING UNPATENTABLE OVER GUO ET AL., U.S. PATENT NO. 6,713,539 BECAUSE *GUO* DOES NOT TEACH, SUGGEST, OR DISCLOSE THAT A METAL SALT OR A METAL OXIDE IMPROVES THE COMPATABILITY OF ASPHALT COMPOSITIONS.**

Claims 1-3, 5-11, 12-20, 23-24, 26, 28, 30-32, 35-37, 39-47, and 49-50 stand rejected under 35 U.S.C. §103(a) as being unpatentable over *Guo et al.*, U.S. 6,713,539. In the Final Rejection, the Examiner relies upon and references the §103(a) rejection that was made in the previous December 12, 2005, Office Action. *See* Final Office Action at Page 3, Par. 2. The December 2005 Office Action states that *Guo* teaches a sulfur crosslinking agents at “column 3 lines 50+” and that the use of the sulfur crosslinking agent in combination with the oxide compounds is rendered obvious by the *Guo* at “column 3 lines 53+” where mixtures of the compounds are identified. *See* 12/12/2005 Office Action at Page 3, Par. 12 – page 4, line 1. The Examiner further states that the incorporation of the ground tire rubber (GTR) is suggested by the dry rubber at “column 3 lines 34+” and that the use of the composition for roads and roofing is obvious from the disclosure at “column 1 lines 13+.” *See* 12/12/2005 Office Action at Page 4, lines 2-4.

However, there is nothing in the *Guo* patent that teaches or suggests the features of the pending claims. First, *Guo* does not teach that adding from about 0.05 wt% up to 5 weight % of a metal salt to an asphalt and polymer composition improves the compatibility of the asphalt and polymer composition as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal salt amount, as recited in the pending claims. *See* Butler Claims 1, 26. *Guo* also does not teach that such compositions have reduced gel, as recited in the pending claims. *See* Butler Claims 14 and 40.

Second, *Guo* does not teach that adding from about 0.05 wt% up to 5 weight % of a metal oxide to an asphalt and polymer composition improves the compatibility of the asphalt and polymer composition as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal oxide amount, as recited in the pending claims. *See* Butler Claim 17 et seq. and Claim 43 et seq.

Third, *Guo* does not teach that adding from about 0.05 wt% up to 5 weight % of a metal oxide selected from Groups IIA and IIB of the Periodic Table to an asphalt, polymer, and ground tire rubber (GTR) composition improves the homogeneity of the asphalt composition as compared with the compatibility of an identical asphalt composition having a lesser metal oxide amount, as recited in the pending claims. See Butler Claim 23 et seq. and Claim 49 et seq.

Fourth, *Guo* does not disclose or suggest Applicants' invention of using metal salts such as zinc oxide, mercaptobenzothiazole (MBT), and the zinc salt of mercaptobenzothiazole (ZMBT) in about 0.05 wt% up to about 5 wt% in order to increase the compatibility of an asphalt and polymer composition. Rather, *Guo* teaches the use of an *organic polar compound* to improve asphalt characteristics. *Guo* states that: "[t]he addition of the cross-linking reagent during the mixing of the asphalt/polymer mother liquor permits the polymer in a good dispersion state to carry out the linking reaction with the organic polar compound in asphalt." (Emphasis added; See Col. 7, lines 7-10). *Guo* states that: "[t]he results of present invention shows that the addition of the organic polar compounds makes the asphalt and the polymer having double bonds form a continuous phase structure through the action of the organic polar compounds.

Further, the *comparative Example 1* in Table 3 of *Guo* shows the preparation of asphalt without the use of a polar solvent, *Guo* teaches the use of a polysulfide -- namely cycloheptathiaimine alkylphenol (see *Guo* Col. 3, lines 63-65); however, that formulation was found to be unstable -- and therefore unsuitable (see *Guo* Col. 9, lines 21-40).

The prior art reference must teach or suggest all of the limitations of the claims. See, *In re Wilson*, 424 F.2d 1382, 1385, 165 U.S.P.Q. 494, 496 (C.C.P.A. 1970.) Thus there is no prima facie case of obviousness. Applicants' method of using from about 0.05 wt% up to 5 weight % of a metal oxide or metal salt to increase the compatibility and the homogeneity of an asphalt composition as compared with the compatibility of an identical asphalt composition having a lesser metal salt amount, is novel and unobvious. This issue is similar to that decided in *Perricone v. Medicis Pharm. Corp.*, 432 F.3d 1368 (Fed. Cir. 2005)<sup>1</sup>. In *Perricone*, the prior art disclosed use of a skin cream to treat

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<sup>1</sup> Although *Perricone* involved the appeal from a trial court decision, the same legal standards apply to the 35 USC § 103 issue in this appeal. One particularly relevant excerpt from that case

damaged and aged skin. The Federal Circuit held that use of the skin cream to treat skin sunburn was patentably new. *Id.* at 1378-1379. Crucial to the court's reasoning was that "skin sunburn" was construed as part of a method step, and this method step was neither disclosed in the prior art nor inherent in it. *Id.* Thus as in *Perricone*, Applicants' claimed invention is not the same method with a new use, but a new method. Similarly to *Perricone*, where the prior art reference was "silent" on the entire subject of sunburn, *Guo* is silent on the subject of using *a metal oxide or metal salt* to increase the compatibility and the homogeneity of an asphalt; thus, Applicants' claims are patentable. *Perricone*, 432 F.3d at 1377. Therefore even in view of *Guo*, Applicants' invention is unobvious and patentable, and such rejections should be reversed.

### Conclusion

In conclusion, the references of record, either or alone or in combination, nowhere teach, show or suggest the features recited in the pending claims. Thus, Appellants respectfully request reversal of the rejections of the pending claims.

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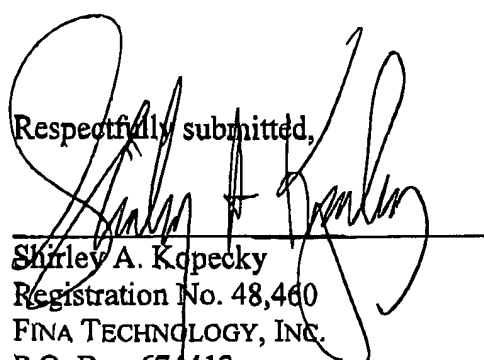
is reproduced below. "The issue is not, as the dissent and district court imply, whether Pereira's lotion *if applied* to skin sunburn would inherently treat that damage, but whether Pereira discloses the application of its composition to skin sunburn. It does not. This court explained in *Catalina Marketing International, Inc. v. Coolsavings.com, Inc.* that a patent to an apparatus does not necessarily prevent a subsequent inventor from obtaining a patent on a new method of using the apparatus. 289 F.3d 801, 809 (Fed.Cir.2002). New uses of old products or processes are indeed patentable subject matter. See 35 U.S.C. § 101 (2000) (identifying as patentable "any new and useful improvements" of a process, machine, manufacture, etc.); *In re King*, 801 F.2d 1324, 1326 (Fed.Cir.1986) (principles of inherency do not prohibit a process patent for a new use of an old structure). That principle governs in this case as well." *Id.* At 1378.

"Claim 1 of the '693 patent recites a new use of the composition disclosed by Pereira, i.e., the treatment of skin sunburn." *Id.* At 1378-79. "The disclosed use of Pereira's lotion, i.e., topical application, does not suggest application of Pereira's lotion to skin sunburn. In other words, the district court's inherency analysis goes astray because it assumes what Pereira neither disclosed nor rendered inherent. Because Pereira does not disclose topical application *to skin sunburn*, this court reverses the district court's holding that Pereira anticipates claims 1-4 and 7 of the '693 patent." *Id.* At 1379.

Dated

March 13, 2007

Respectfully submitted,

  
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**Appendix A**  
***Pending Claims***

**Listing of claims:**

We Claim:

1. (Previously Presented) A method for preparing asphalt and polymer compositions comprising:  
heating a mixture consisting essentially of asphalt and an elastomeric polymer;  
adding from about 0.05 wt% up to 5 weight % of a metal salt based on the weight of the asphalt/polymer mixture, where the metal of the metal salt is selected from the group consisting essentially of zinc, cadmium, mercury, copper, silver, nickel, platinum, iron, magnesium, and mixtures thereof; and  
where the compatibility of the asphalt and polymer composition is improved as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal salt amount.
2. (Previously Presented) The method of claim 1 where the metal salt is a metal oxide.
3. (Original) The method of claim 1 where the metal salt is a metal oxide selected from the group consisting of zinc oxide, calcium oxide and combinations thereof.
4. (Cancelled).
5. (Cancelled).
6. (Previously Presented) The method of claim 1 further comprising adding a crosslinker to the mixture.

7. (Previously Presented) The method of claim 6 where in adding the crosslinker, the crosslinker is selected from the group consisting essentially of elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof.
8. (Original) The method of claim 6 where the metal salt proportion is at least about five times greater than the crosslinker proportion.
9. (Original) The method of claim 6 where the crosslinker is present in an amount ranging from about 0.01 to 0.4 wt%, based on the weight of the asphalt/polymer mixture.
10. (Original) The method of claim 1 further comprising adding ground tire rubber (GTR) to the mixture of asphalt and an elastomeric polymer.
11. (Previously Presented) The method of claim 10 where the GTR ranges from about 1 to about 20 wt% of the mixture.
12. (Cancelled).
13. (Previously Presented) The method of claim 10 where the GTR and mixture of asphalt and an elastomeric polymer is more homogeneous as compared to an identical mixture of GTR, asphalt and elastomeric polymer having a lesser amount of metal salt.
14. (Original) The method of claim 1 where the asphalt and polymer compositions have reduced gel.
15. (Previously Presented) A method of road building comprising combining the asphalt and polymer compositions made by the method of claim 1 with an aggregate to form a road paving material, and using the material to form road pavement.

16. (Previously Presented) A method of sealing a roof comprising heating the asphalt and polymer compositions made by the method of claim 1 and distributing it over at least a portion of a roof surface.

17. (Previously Presented) A method for preparing asphalt and polymer compositions comprising:

heating a mixture consisting essentially of asphalt and an elastomeric polymer;  
adding a metal oxide, where the metal oxide is selected from the group consisting essentially of zinc oxide, iron oxide, copper oxide, magnesium oxide calcium oxide and combinations thereof, and where the metal oxide is added in an amount at least from about 0.05 wt% up to 5 wt % based on the weight of the asphalt/polymer mixture; and  
where the compatibility of the asphalt and polymer composition is improved as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal oxide amount.

18. (Previously Presented) The method of claim 17 where the metal oxide is zinc oxide.

19. (Previously Presented) The method of claim 17 further comprising adding a crosslinker to the mixture.

20. (Previously Presented) The method of claim 19 where in adding the crosslinker, the crosslinker is selected from the group consisting of elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof.

21. (Cancelled).

22. (Cancelled).

23. (Previously Presented) A method for preparing asphalt and polymer compositions comprising:

heating a mixture consisting essentially of asphalt and an elastomeric polymer;

adding from about 0.05 wt% up to 5 wt% of a metal oxide, where the metal of the metal oxide is selected from Groups IIA and IIB of the Periodic Table (CAS notation);

adding ground tire rubber (GTR) to the mixture of asphalt and elastomeric polymer before or after the metal oxide is added; and

where the GTR and mixture of asphalt and elastomeric polymer is more homogeneous as compared to an identical mixture of GTR, asphalt and elastomeric polymer having a lesser amount of metal oxide.

24. (Previously Presented) The method of claim 23 where the GTR ranges from about 1 to about 20 wt% of the mixture.

25. (Cancelled).

26. (Previously Presented) A polymer modified asphalt (PMA) consisting essentially of:

an asphalt;

an elastomeric polymer; and

an organic or inorganic metal salt present in an amount from about 0.05 wt% up to 5 wt% based on the weight of the asphalt/polymer mixture, where the metal of the metal oxide is selected from the group consisting essentially of zinc, cadmium, mercury, copper, silver, nickel, platinum, iron, magnesium, and mixtures thereof.

27. (Cancelled).

28. (Original) The PMA of claim 26 where the metal salt is a metal oxide selected from the group consisting of zinc oxide, calcium oxide and combinations thereof.



29. (Cancelled).
30. (Previously Presented) The PMA of claim 26 where the compatibility of the PMA is improved as compared with the compatibility of an identical PMA having a lesser metal salt amount.
31. (Previously Presented) The PMA of claim 26 further consisting of a crosslinker.
32. (Previously Presented) The PMA of claim 31 where the crosslinker is selected from the group consisting of elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof.
33. (Cancelled).
34. (Cancelled).
35. (Previously Presented) The PMA of claim 26 further consisting of ground tire rubber (GTR).
36. (Previously Presented) The PMA of claim 35 where the GTR ranges from about 1 to about 20 wt% of the PMA.
37. (Previously Presented) The PMA of claim 35 where the metal salt is zinc oxide.
38. (Cancelled).
39. (Previously Presented) The PMA of claim 35 where the mixture of GTR and PMA is more homogeneous as compared to an identical mixture of GTR and PMA having a lesser amount of metal salt.
40. (Original) The PMA of claim 26 where the PMA has reduced gel.

41. (Original) A road made from the PMA of claim 26 and aggregate.
42. (Original) A roof sealed with the PMA of claim 26.
43. (Previously Presented) A polymer modified asphalt (PMA) consisting essentially of:
- asphalt;
  - an elastomeric polymer;
  - a metal oxide present in an amount at least from about 0.05 wt% up to 5 wt% based on the weight of the asphalt/polymer mixture, where the metal oxide is selected from the group consisting essentially of zinc oxide, calcium oxide and combinations thereof; and
  - where the compatibility of the asphalt and polymer composition is improved as compared with the compatibility of an identical asphalt and polymer composition having a lesser metal oxide amount.
44. (Original) The PMA of claim 43 where the metal oxide is zinc oxide and the zinc oxide is present in an amount ranging from about 0.05 to about 2 wt.% based on the combined amount of asphalt and elastomeric polymer.
45. (Previously Presented) The PMA of claim 43 further consisting of a crosslinker.
46. (Previously Presented) The PMA of claim 45 where the crosslinker is selected from the group consisting of elemental sulfur, mercaptobenzothiazole (MBT), thiurams, mercaptobenzimidazole, and mixtures thereof.
47. (Original) The PMA of claim 45 where the metal oxide proportion is at least about five times greater than the crosslinker proportion.
48. (Cancelled).

49. (Previously Presented) A polymer modified asphalt (PMA) consisting essentially of:

a mixture of asphalt and an elastomeric polymer;

a metal oxide in an amount at least 0.05 wt% up to 5 wt% based on the weight of the asphalt/polymer mixture, where the metal of the metal oxide is selected from Groups IIA and IIB of the Periodic Table (CAS notation), and where the elastomeric polymer is ground tire rubber (GTR); and

where the GTR and mixture of asphalt and an elastomeric polymer is more homogeneous as compared to an identical mixture of GTR, asphalt and elastomeric polymer having a lesser amount of metal oxide.

50. (Previously Presented) The PMA of claim 49 where the GTR ranges from about 1 to about 20 wt% of the mixture.

51. (Cancelled).

**Appendix B*****Evidence***

1. U.S. Patent No. 6,713,539 (*Guo et al.*).



US006713539B2

(12) **United States Patent**  
Guo et al.

(10) Patent No.: **US 6,713,539 B2**  
(45) Date of Patent: **Mar. 30, 2004**

(54) **STORAGE-STABLE MODIFIED ASPHALT COMPOSITION AND ITS PREPARATION PROCESS**

(75) Inventors: Shuhua Guo, Beijing (CN); Weiql Huang, Beijing (CN); Jun Long, Beijing (CN); Baichun Zhang, Beijing (CN); Zijun Wang, Beijing (CN); Yucheng She, Beijing (CN)

(73) Assignees: China Petroleum & Chemical Corporation, Beijing (CN); Research Institute of Petroleum Processing, Sinopec, Beijing (CN)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 193 days.

(21) Appl. No.: 09/931,846

(22) Filed: Aug. 17, 2001

(65) **Prior Publication Data**

US 2002/0068776 A1 Jun. 6, 2002

(30) **Foreign Application Priority Data**

Aug. 18, 2000 (CN) ..... 00123512 A  
Aug. 18, 2000 (CN) ..... 00123513 A

(51) Int. Cl.<sup>7</sup> ..... C08L 95/00

(52) U.S. Cl. .... 524/68; 524/59; 524/70

(58) Field of Search ..... 524/59, 68, 70

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Primary Examiner—Peter Szekely

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(57) **ABSTRACT**

A storage-stable modified asphalt composition, which comprises: 50-97.7 parts by weight of a base asphalt, 2.0-20.0 parts by weight of a polymer having double bonds, 0.1-20.0 parts by weight of a compatibilizer, 0.1-10.0 parts by weight of a cross-linking reagent, and 0.1-10.0 parts by weight of an organic polar compound, and the softening point difference of its product determined by the stability test is lower than 2.5° C. The process for preparing said modified asphalt composition is mixing 50-97.7 parts by weight of a base asphalt, 2.0-20.0 parts by weight of a polymer having double bonds, 0.1-20.0 parts by weight of a compatibilizer 0.1-10.0 parts by weight of a cross-linking reagent, and 0.1-10.0 parts by weight of an organic polar compound under certain conditions. The modified asphalt provided by the present invention has good storage-stability. The preparation process provided by the present invention is simple, and there is no need for special apparatus.

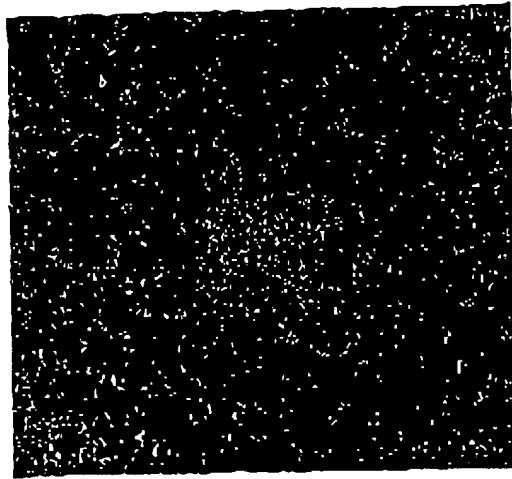
34 Claims, 1 Drawing Sheet

**U.S. Patent**

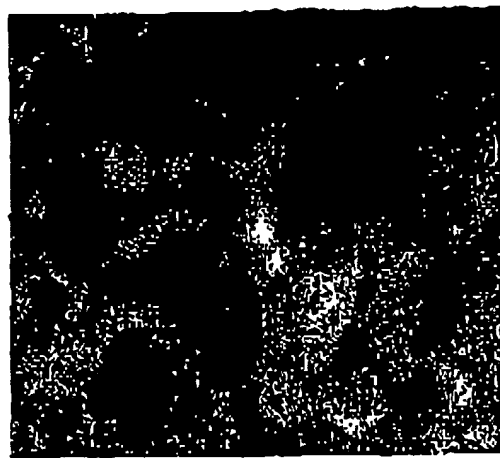
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**Fig. 1**



**Fig.2.**

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STORAGE-STABLE MODIFIED ASPHALT  
COMPOSITION AND ITS PREPARATION  
PROCESS

## FIELD OF THE INVENTION

The present invention is related to an asphalt composition and its preparation process. More particularly, it is related to a storage-stable polymer-modified asphalt composition and its preparation process.

## DESCRIPTION OF THE PRIOR ART

Asphalt materials have rapidly developed as paving and decorating materials in the road and architecture sectors. However, the optimum performance properties of asphalt and its blend such as viscoelasticity, plasticity, adhesiveness, etc. can not exert since they are affected by many factors. Among various factors, climate is the most important one. In the season of high temperature, summer, ruts caused by racing vehicles on express highways are the major factor leading to the damage of the road surface. In winters, fractures on the road surface resulted from the abruptly change of the temperature are the major causes for the transverse crack. In the rain seasons in the south, the intrusion of the rainwater leads to the interaction of asphalt with the blend material at the interface, thereby lowering the adhesive performance of asphalt and making it easy for asphalt to strip from the stones. Therefore, it is necessary to improve the Theological property of asphalt. Addition of a polymer is an effective way to improve the performance of asphalt. Addition of a polymer can enhance the viscosity and high temperature resistance, lower the low temperature sensibility, and improve the low temperature performance at the same time.

Asphalt modified by olefin polymers is reviewed in T. F. Yen, et al., *Asphaltenes and Asphalts, I Developments in Petroleum Science*. The amount of the polymers is 6 wt %, and the stability of asphalt modified by various polymers is shown in Table 1.

TABLE 1

Polymer type	Nons	APP	LDPE	EPDM	SBS
Penetration (25° C., 100 g. 5 s), dmm	133	145	41	50	72
Softening point (ring-and-ball), ° C.	44	47	98	66	78
Stability Test Top softening point, ° C.	—	55	>100	87	>100
(163° C., 48 h) Bottom softening point, ° C.	—	45	52	52	61
Softening point difference, ° C.	—	10	>50	35	>40

It can be seen from Table 1 that when APP (atactic polypropylene), LDPE (low density polyethylene), EPDM (ethylene-propylene-diene ternary copolymer), SBS (styrene-butadiene-styrene three-block copolymer) are added to asphalt respectively, phase separation takes place between most of the polymers and asphalt, thus directly affecting the performance properties of the asphalt-polymer compositions.

EP 639630A1 discloses a process for preparing stable asphalt-polymer compositions, wherein a raw asphalt with a certain constitution is first screened as the raw material of the modified asphalt, and then reacted with the three block polymer SBS as a polymer modifier and a vinyl aromatic

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(such as styrene) as an assistant added thereto in an inert environment to yield a sample with good stable performance. There is a limit to the source of the raw material of the modified asphalt in this process, and styrene as an assistant is of no help in the dispersion of SBS in asphalt. In addition, the reaction cost increases since a nitrogen environment is needed.

U.S. Pat. Nos. 5,336,705, 5,627,225, and 5,348,994 first use fuming sulfuric acid or other sulfonating reagent to sulfonate the raw asphalt and the polymer modifier to incorporate acidic groups into both of them, and then neutralize with alkalis such as CaO, ZnO, etc. as neutralization reagents. This process prolongs the preparation process, increases the production cost, and results in corrosion of the apparatus by sulfonating reagents.

U.S. Pat. No. 5,306,750 discloses a process for reacting a polymer with asphalt, and a polymer-linked-asphalt product. This process is to covalently react 0.05–2 wt % of an epoxide-containing polymer with asphalt at a temperature above 100° C. for longer than 1 h. No phase separation happened with the modified asphalt obtained by this process after storing in a drying oven at 163° C.–177° C. for 4 days.

U.S. Pat. No. 5,331,028 discloses a polymer-modified asphalt composition and its preparation process. The constitution of the composition is that the reaction product derived by the reaction between 100 parts by weight of asphalt and 0.5–11 parts by weight of an ethylene copolymer containing glycidyl accounts for 80–99.7 wt %, and that the styrene/conjugated diene block copolymer accounts for 0.3–20 wt %. The process is to mix 70–99.2 wt % of asphalt, 0.5–10 wt % of the ethylene copolymer containing glycidyl, and 0.3–20 wt % of a styrene/conjugated diene block copolymer, and to react at 170° C.–220° C. for 6–36 h to yield a reaction product.

Although the compatibility of the polymer with asphalt used in U.S. Pat. Nos. 5,331,028 and 5,306,750 is rather good, the high preparation cost of the polymer and the difficulty in reaction are the major control factors.

One of the objectives of the present invention is to provide a storage-stable modified asphalt composition.

Another objective of the present invention is to provide a process for preparing the storage-stable modified asphalt composition.

## SUMMARY OF THE INVENTION

The present invention provides a storage-stable modified asphalt composition, which comprises:

base asphalt	50–97.7 parts by weight;
polymer having double bonds	2.0–20.0 parts by weight;
compatibilizer	0.1–20.0 parts by weight;
cross-linking reagent	0.1–10.0 parts by weight;
organic polar compound	0.1–10.0 parts by weight;

and the softening point difference of its product determined by the stability test is lower than 2.5° C.

The present invention also provides a process for preparing the storage-stable modified asphalt composition, which comprises mixing 50–97.7 parts by weight of a base asphalt, a 2.0–20.0 parts by weight of a polymer having double bonds, 0.1–20.0 parts by weight of a compatibilizer, 0.1–10.0 parts by weight of a cross-linking reagent, and 0.1–10.0 parts by weight of an organic polar compound under certain conditions.

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## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a storage-stable modified asphalt composition, which comprises:

base asphalt	50-97.7 parts by weight;
polymer having double bonds	2.0-20.0 parts by weight;
compatibilizer	0.1-20.0 parts by weight;
cross-linking reagent	0.1-10.0 parts by weight;
organic polar compound	0.1-10.0 parts by weight;

and the softening point difference of its product determined by the stability test is lower than 2.5° C.

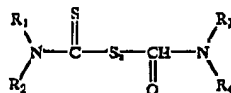
Said base asphalt is one selected from the group consisting of petroleum asphalts, coal-tar asphalts, tar sand asphalts and native asphalts, or a mixture thereof, wherein the petroleum asphalt is one selected from the group consisting of straight-run asphalt, asphalt obtained by solvent deasphalting, oxidized asphalts, and blended asphalts, or a mixture thereof. Said straight-run asphalt is an atmospheric residue or vacuum residue obtained through atmospheric distillation or vacuum distillation, the Penetration of which at 25° C. is 20-300 dmm (i.e. 1/6mm). Said asphalt obtained by solvent deasphalting is a deoiled asphalt obtained by extracting a residue with one of the C<sub>3</sub>-C<sub>5</sub> hydrocarbons or their mixtures. The Penetration of the deoiled asphalt at 25° C. is 5-200 dmm.

Said polymer having double bonds is a block polymer of styrene-butadiene in a ratio of 20-45:80-55 which mainly refers to the SBS type. The structure of SBS is star or linear, the molecular weight of which is in the range of 100,000 to 350,000. The block polymer can be either a dry rubber, or an oil-extended polymer wherein 2-60 wt % weight of oil is extended.

Said compatibilizer is one selected from the group consisting of styrene tar, tall oil, acid-containing tall oil, catalytically cracked oil slurry, heavy deasphalted oil, extracted oil obtained by solvent refining, naphthenic acid, naphthenic oil, white oil, and coal tar fractions, or a mixture thereof.

Said cross-linking reagent is one selected from the group consisting of crystallized sulfurs, activated sulfurs, sulfur-donors, and "symbolizing" sulfur-donating cross-linking reagents, or a mixture thereof. Said activated sulfur is a sulfur powder, a colloidal sulfur, or a mixture thereof. Said colloidal sulfur is a colloid with an average diameter of 1-5 μm prepared by mixing sulfur powder or precipitated sulfur with a dispersion reagent and then grinding. The sulfur donor is one selected from the group consisting of sulfur-containing morpholinium compounds, thiuram compounds, and polysulfides, or a mixture thereof.

The general formula of the thiuram compounds is:



wherein x=1-4, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub>: a C<sub>1</sub>-C<sub>4</sub> alkyl.

Polysulfides: R<sub>1</sub>-(S)<sub>x</sub>-R<sub>2</sub>, R<sub>1</sub>, R<sub>2</sub> is a aliphatic or aromatic heterocyclic group, such as cycloheptathisimine alkylphenol, alkylphenol monosulfide.

Said "symbolizing" sulfur-donating cross-linking reagent mainly refers to a metal oxide cross-linking reagent, wherein

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the metal mainly refers to a divalent metal such as Ca, Mg, Zn or Pb, etc. Said "symbolizing" sulfur-donating cross-linking reagent is one selected from the group consisting of CaO, MgO, ZnO, and PbO, or a mixture thereof.

Said organic polar compound mainly refers to a compound with polar groups, which is one selected from the group consisting of amine, acid, phenolic resin and aldehyde compounds, or a mixture thereof.

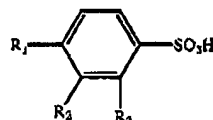
Said amine compounds mainly refer to aliphatic amine and aromatic amine compounds, which is one selected from polyacene polyamine compounds, wherein the polyacene comprises di-, tri- and tetraethylene; and the polyamine comprises hexamethylene diamine, tetramine, penta-amine, or a mixture thereof.

Said acid compound is one selected from the group consisting of carboxylic acid, acid anhydride, sulfonic acid, boric acid, and phosphoric acid compounds, or a mixture thereof.

Said carboxylic acid compound is one selected from the group consisting of aliphatic acids and aromatic acids, or a mixture thereof.

Said acid anhydride compounds are phthalic anhydride and its derivatives or maleic anhydride and its derivatives.

The general formula of said sulfonic compounds is:



wherein R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> is a C<sub>1</sub>-C<sub>5</sub> alkyl.

Said phosphoric acid compound is one selected from polyphosphoric acid, phosphorous acid, modified polyphosphoric acid, and phosphate compounds, or a mixture thereof.

Said phenolic resin compound is one selected from formaldehyde alkylphenol resin compounds, wherein the alkyl is p-tert-butyl or p-tert-octyl paraffinic group. The polar hetero-atom containing alkyl is also desired, wherein said formaldehyde alkylphenol resin comprises formaldehyde phenol resin having sulfur or oxygen atom containing alkyl.

Said aldehyde compound is one selected from glycidic aldehyde, formaldehyde, binary aldehydes, and furfural, or a mixture thereof, wherein the binary aldehydes are p-phthalic aldehyde and its derivatives or m-phthalic aldehyde and its derivatives.

The present invention also provides the process for preparing a storage-stable modified asphalt composition, which comprises: mixing 50-97.7 parts by weight of a base asphalt, 2.0-20.0 parts by weight of a polymer having double bonds, 0.1-20.0 parts by weight of a compatibilizer, 0.1-10.0 parts by weight of a cross-linking reagent, and 0.1-10.0 parts by weight of an organic polar compound under certain conditions.

Said compatibilizer can be first mixed with the base asphalt, or with the polymer having double bonds, or with the mixture of the polymer having double bonds and the base asphalt; or said compatibilizer can be added at last, said compatibilizer can be added either once or twice. Said base asphalt can also be added either once or twice.

Mixing of various components can be static, dynamic, grinding, or vigorous stirring.

The process provided by the present invention will be illustrated below with four embodiments, but the process provided by the present invention is not limited to the three embodiments.



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## Embodiment 1:

The process provided by the present invention comprises the following steps:

- (1) contacting the base asphalt with the compatibilizer at 100° C.-250° C. for 0.1-6 h to yield the treated base asphalt;
- (2) mixing the treated base asphalt with the polymer having double bonds for 0.1-10 h to yield the asphalt mother liquor;
- (3) adding the cross-linking reagent, organic polar compound, and optional base asphalt to the asphalt mother liquor at 100° C.-250° C. to react for 5-300 min, yielding the modified asphalt composition.

In this embodiment, said base asphalt, polymer having double bonds, compatibilizer, cross-linking reagent, and organic polar compound account for 50-97.7 parts by weight, 2.0-20.0 parts by weight, 0.1-20.0 parts by weight, 0.1-10.0 parts by weight, and 0.1-10.0 parts by weight of the modified asphalt composition, respectively. The weight ratio of the base asphalt in step (3) to that in step (1) is 0-50:100-50.

## Embodiment 2:

The process provided by the present invention comprises the following steps:

- (1) contacting the base asphalt with the compatibilizer at 100° C.-250° C. for 0.1-6 h to yield the treated base asphalt;
- (2) mixing the treated base asphalt with the polymer having double bonds for 0.1-10 h to yield the asphalt mother liquor;
- (3) adding the cross-linking reagent, organic polar compound, and optional compatibilizer to the asphalt mother liquor at 100° C.-250° C. to react for 5-300 min, yielding the modified asphalt composition.

In this embodiment, said base asphalt, polymer having double bonds, compatibilizer cross-linking reagent, and organic polar compound account for 50-97.7 parts by weight, 2.0-20.0 parts by weight, 0.1-20.0 parts by weight, 0.1-10.0 parts by weight, and 0.1-10.0 parts by weight of the modified asphalt composition. The weight ratio of the compatibilizer in step (3) to that in step (1) is 0-50:100-50.

## Embodiment 3:

The process provided by the present invention comprises the following steps:

- (1) mixing the base asphalt at 100° C.-250° C. with the polymer having double bonds for 0.1-10 h to yield the asphalt mother liquor;
- (2) contacting the asphalt mother liquor at 100° C.-250° C. with the compatibilizer at 100-250° C. for 0.1-6 h to yield the treated asphalt mother liquor;
- (3) adding the cross-linking reagent, organic polar compound, and the optional base asphalt to the treated asphalt mother liquor to react for 5-300 min, yielding the modified asphalt composition.

In this embodiment, said base asphalt, polymer having double bonds, compatibilizer, cross-linking reagent, and organic polar compound account for 50-97.7 parts by weight, 2.0-20.0 parts by weight, 0.1-20.0 parts by weight, 0.1-10.0 parts by weight, and 0.1-10.0 parts by weight of the modified asphalt composition, respectively. The weight ratio of the base asphalt in step (3) to that in step (1) is 0-50:100-50.

## Embodiment 4:

The process provided by the present invention comprises the following steps:

- (1) contacting 2.0-20.0 parts by weight of a polymer having double bonds with 0.1-20.0 parts by weight of

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a, compatibilizer at 10° C.-250° C. for 0.1-72 h to yield the treated polymer having double bonds;

- (2) heating 50-97.7 parts by weight of the base asphalt to 100° C.-250° C.;
- (3) mixing the treated polymer having double bonds with the heated base asphalt for 0.1-6.0 h to yield an asphalt mother liquor, and maintaining the temperature of the asphalt mother liquor at 100° C.-250° C.;
- (4) adding 0.1-10.0 parts by weight of the cross-linking reagent and 0.1-10.0 parts by weight of the organic polar compound into the asphalt mother liquor to react for 5-300 min, yielding the modified asphalt composition.

Said base asphalt in the aforesaid process is one selected from the group consisting of petroleum asphalts, coal-tar asphalts, tar sand asphalts and native asphalts, or a mixture thereof, wherein the petroleum asphalt is one selected from the group consisting of straight-run asphalts, asphalts obtained by solvent deasphalting, oxidized asphalts, and blended asphalts, or a mixture thereof. The straight-run asphalt is an atmospheric residue or vacuum residue obtained through atmospheric distillation or vacuum distillation, the Penetration of which at 25° C. is 20-300 dmm (i.e. 1/10 mm). The asphalt obtained by solvent deasphalting is a deoiled asphalt obtained by extracting a residue with one of the C<sub>3</sub>-C<sub>8</sub> hydrocarbons or their mixtures. The Penetration of the deoiled asphalt at 25° C. is 5-200 dmm.

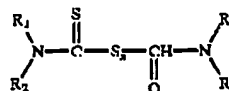
Said polymer having double bonds is a block polymer of styrene-butadiene in a ratio of 20-45:80-55, which mainly refers to the SBS polymers. The structure of the SBS is the star or linear, the molecular weight of which is in the range of 100,000 to 350,000. The block polymer can be either a dry rubber, or an oil-extended polymer wherein 2-60 wt % of oil is extended.

Said compatibilizer is one selected from the group consisting of styrene tar, tall oil, acid-containing tall oil, catalytically cracked oil slurry, heavy deasphalted oil, extracted oil obtained by solvent refining, naphthenic acid, naphthenic oil, white oil, and coal tar fractions, or a mixture thereof.

The addition of the compatibilizer into the system can enhance the compatibility of the polymer in asphalt. Since the compatibilizer itself has good intersolubility with both the polymer and asphalt, it can increase the compatibility with both.

Said cross-linking reagent is one selected from the group consisting of crystallized sulfurs, activated sulfurs, sulfur-donors, and "symbolizing" sulfur-donating cross-linking reagents, or a mixture thereof. Said activated sulfur is a sulfur powder, a colloidal sulfur, or a mixture thereof. Said colloidal sulfur is a colloid with an average diameter of 1-5 μm prepared by mixing sulfur powder or precipitated sulfur with a dispersion reagent and then grinding. The sulfur donor is one selected from the group consisting of sulfur-containing morpholinium compounds, thiuram compounds, and polysulfides, or a mixture thereof.

The general formula of the thiuram type compounds is:



wherein x=1-4, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub>: a C<sub>1</sub>-C<sub>4</sub> alkyl.

Polysulfides: R<sub>1</sub>-(S)<sub>n</sub>-R<sub>2</sub>, R<sub>1</sub>, R<sub>2</sub> is an aliphatic or aromatic heterocyclic group, such as cycloheptathiazimine alkylphenol, alkylphenol monosulfide.

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The "symbolizing" sulfur-donating cross-linking reagent mainly refers to a metal oxide cross-linking reagent, wherein the metal mainly refers to a divalent metal such as Ca, Mg, Zn, Pb, etc. Said "symbolizing" sulfur-donating cross-linking reagent is one selected from one of the group consisting of CaO, MgO, ZnO, and PbO, or a mixture thereof.

The addition of the cross-linking reagent during the mixing of the asphalt/polymer mother liquor permits the polymer in a good dispersion state to carry out the linking reaction with the organic polar compound in asphalt. Thus, the polymer can exist in a stable network structure, and the further aggregation and stability of the polymer are prevented.

Said organic polar compound mainly refers to a compound with polar groups, which is one selected from the group consisting of amine, acid, phenolic resin and aldehyde compounds, or a mixture thereof.

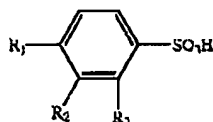
Said amine compounds mainly refer to aliphatic amine and aromatic amine compounds which is one selected from polyactene polyamine compounds, wherein the polyactene comprises di-, tri- and tetraethylene; and the polyamine comprises hexamethylene diamine, tetramine, penta-amine, or a mixture thereof.

Said acid compound is one selected from the group consisting of carboxylic acid, acid anhydride, sulfonic acid, boric acid, and phosphoric acid compounds, or a mixture thereof.

Said carboxylic acid compound is one selected from the group consisting of aliphatic acids and aromatic acids, or a mixture thereof.

Said acid anhydride compounds are phthalic anhydride and its derivatives or maleic anhydride and its derivatives.

The general formula of said sulfonic compounds is:



$R_1, R_2, R_3 = H$  or a  $C_1-C_3$  alkyl

Said phosphoric acid compound is one selected from polyphosphoric acid, phosphorous acid, modified polyphosphoric acid, and phosphate compounds, or a mixture thereof.

Said phenolic resin compound is one selected from formaldehyde alkylphenol resin compounds, wherein the alkyl is *p*-tert-butyl or *p*-tert-octyl paraffinic group. The polar hetero-atom containing alkyl is also desired, wherein said formaldehyde alkylphenol resin comprises formaldehyde phenol resin having sulfur or oxygen atom containing alkyl.

Said aldehyde compound is one selected from the group consisting of glycidic aldehyde, formaldehyde, binary aldehydes, and furfural, or a mixture thereof, wherein the binary aldehydes are *p*-phthalic aldehyde and its derivatives or *m*-phthalic aldehyde and its derivatives.

The function of adding organic polar compounds in the present system is to promote the reaction of the cross-linking reagent. The results of present invention shows that the addition of the organic polar compounds makes the asphalt and the polymer having double bonds form a continuous phase structure through the action of the organic polar compounds.

The modified asphalt composition prepared by the process provided by the present invention has good storage-stability, its softening point difference determined by the stability method being lower than  $2.5^\circ C$ . The preparation process

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provided by the present invention is simple and needs no special apparatus. The modified asphalt composition can be directly used in rainy and wet areas without using anti-stripping reagents to increase the adhesive capability between the stone and asphalt since it has a high viscosity, adhesives, and strong wrap ability for stone. The modified asphalt composition prepared by the process provided by the present invention can also be used as a basic raw material of emulsified asphalt, which may be realized by adding a certain proportion of water and an emulsifier.

## DESCRIPTION OF THE DRAWINGS

FIG. 1 is an electronic microscope image of a modified asphalt composition of one example of the present invention;

FIG. 2 is an electronic microscope image of a modified asphalt composition of one comparative example.

The modified asphalt composition and the process provided by the present invention will be further illustrated below in combination with the examples, but the present invention is not limited thereby.

## EXAMPLES

Base asphalt A and B used in the present invention were a straight-run asphalt and a asphalt by propane deasphalting, the properties of which are shown in Table 2. The SRS polymer was 1403 produced by Beijing Yanshan Petrochemical Co. The colloidal mill was FD3/60-20 produced by Shanghai Fluko Electromechanical Equipment Co. Stability test was made according to the method provided by ASTM D 5892-96a, and the softening point was determined according to the method provided by GB/T 4507.

## Example 1

The present example illustrates the case wherein the modified asphalt composition was prepared by treating the base asphalt with the compatibilizer.

First, to 360 g of base asphalt A at  $190^\circ C$ . is added 120 g of acid-containing tall oil (produced by Liaoning Petrochemical Fiber Plant, the same below), and the mixture was mixed at  $180^\circ C$ . for 1 h. Then to the treated base asphalt A were added in sequence 90 g of SBS, 18 g of colloidal sulfur (produced by Maoming Petrochemical Co. the same below), and 12 g of maleic anhydride (produced by Lanzhou Chemical Industry Co., the same below), and the mixture was reacted at  $120^\circ C$ . for 6 h, yielding the modified asphalt composition, the properties of which are shown in Table 3. It can be seen from Table 3 that the softening point difference determined by the stability test is only  $2^\circ C$ .

## Example 2

The present example illustrates the case wherein the modified asphalt composition was prepared by adding the compatibilizer twice.

First, to 360 g of base asphalt A at  $190^\circ C$ . is added 60 g of acid-containing tall oil, and the mixture was mixed at  $180^\circ C$ . for 1 h. Then to the treated base asphalt A were added in sequence 90 g of SBS, 18 g of colloidal sulfur, 12 g of maleic anhydride, and 60 g of acid-containing tall oil, and the mixture was reacted at  $220^\circ C$ . for 6 h, yielding the modified asphalt composition, the properties of which are shown in Table 3. It can be seen from Table 3 that the softening point difference determined by the stability test is only  $2.5^\circ C$ .

## Example 3

The present example illustrates the case wherein the modified asphalt composition was prepared by treating the asphalt mother liquor with the compatibilizer.

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470.3 g of base asphalt A at 160° C. is mixed with 14.3 g of SBS for 2.0 h, yielding 484.6 g of an asphalt mother liquor. To the asphalt mother liquor at 120° C. was added 4.9 g of styrene tar, and the mixture was mixed at 180° C. for 0.5 h, yielding a treated asphalt mother liquor. To the treated asphalt mother liquor were added 0.5 g of cyclophosphorothioimine (produced by Lanzhou Chemical Industry Co., the same below) and 10 g of polyphosphoric acid (produced by Jilin Chemical Industry Co., the same below), and the mixture was reacted for 150 min, yielding the modified asphalt composition, the properties of which are shown in Table 3. The microstructure of the modified asphalt composition can be identified by the image of the microscope. It can be seen from Table 3 that the softening point difference determined by the stability test is only 1° C. FIG. 1 shows the SBS polymer distributed uniformly in the modified asphalt composition, and the polymer forming a continuous phase, that means the modified asphalt composition is very stable.

## Comparative Example 1

Compared to Example 3, no organic polar compound is added in the present comparative example.

479.7 g of base asphalt A at 200° C. is mixed with 14.3 g of SBS for 0.5 h, yielding 494.0 g of an asphalt mother liquor. To the asphalt mother liquor at 120° C. was added 5.0 g of styrene tar, and the mixture was mixed at 200° C. for 0.5 h, yielding a treated asphalt mother liquor. To the treated asphalt mother liquor was added 0.5 g of cyclophosphorothioimine, and the mixture was reacted for 150 min, yielding the modified asphalt composition. The microstructure of the modified asphalt composition can be identified by the image of the microscope. Its properties are shown in Table 3. It can be seen from Table 3 that the softening point difference determined by the stability test is as high as 45° C. FIG. 1 shows the SBS polymer distributed in the modified asphalt composition in flocculation state; the asphalt forming a continuous phase, and the polymer having the tendency to aggregate, that means the modified asphalt composition is not stable.

## Example 4

The present example illustrates the case wherein the modified asphalt composition was prepared by treating the asphalt mother liquor with the compatibilizer.

436.5 g of base asphalt A at 150° C. is mixed with 13.5 g of SBS for 3.0 h, yielding 450 g of asphalt mother liquor. To the asphalt mother liquor at 150° C. was added 90 g of white oil, and the mixture was mixed at 150° C. for 0.5 h, yielding a treated asphalt mother liquor. To the treated asphalt mother liquor were added 30 g of zinc oxide (produced by Huangyan Chemical Plant, Jiangsu) and 30 g of hexamethylene diamine (produced by Lanzhou Chemical Industry Co.), and the mixture was reacted for 60 min, yielding the modified asphalt composition, the properties of which are shown in Table 4. It can be seen from Table 4 that the softening point difference determined by the stability test is only 0.5° C.

## Example 5

The operation procedure, operation conditions, and the contents of various components in Example 5 are the same as those in Example 4, except that base asphalt A is replaced by base asphalt B. The properties of the prepared modified asphalt composition are shown in Table 4. It can be seen from Table 4 that the softening point difference determined by the stability test is only 0.5° C.

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## Example 6

The present example illustrates the case wherein the modified asphalt composition was prepared by adding the base asphalt twice.

379.8 g of base asphalt A at 180° C. is mixed with 14.7 g of SBS for 2.0 h, yielding 394.5 g of an asphalt mother liquor. To the asphalt mother liquor at 180° C. was added 2.5 g of catalytically cracked oil slurry, and the mixture was mixed at 180° C. for 0.5 h, yielding a treated asphalt mother liquor. To the treated asphalt mother liquor were added 5 g of disulfurized dimorpholine (produced by Jilin Chemical Industry Co.), 3 g of a mixture of polyphosphoric acid and glycidic aldehyde (produced by Jilin Chemical Industry Co.), and 95.0 g of base asphalt A, and the mixture was mixed at 180° C. for 0.5 h, yielding the modified asphalt composition. The properties of which are shown in Table 4. It can be seen from Table 4 that the softening point difference determined by the stability test is only 2° C.

## Example 7

The present example illustrates the case wherein the modified asphalt composition was prepared by adding the compatibilizer at last.

474.8 g of base asphalt A at 185° C. is first mixed with 14.7 g of SBS for 2.0 h, yielding 489.5 g of an asphalt mother liquor. To the asphalt mother liquor at 180° C. was added in sequence a mixture of 5 g of disulfurized tetrabutyl thiuram (produced by Qingdao Chemical Plant, Shandong) and 3 g of p-toluenesulfonic acid (produced by Nanjing Huajing Group Co.), and 2.5 g of catalytically cracked oil slurry, and the mixture was mixed at 180° C. for 0.5 h, yielding the modified asphalt composition, the properties of which are shown in Table 4. It can be seen from Table 4 that the softening point difference determined by the stability test is only 1° C.

## Example 8-11

Example 8-11 illustrate the case wherein the modified asphalt compositions were prepared by treating polymer having double bonds with different kinds of compatibilizers.

## Example 8

A35 g of SBS was contacted with 75 g of the heavy deasphalted oil at 180° C. for 2 h, and then to the treated SBS were added 385 g of base asphalt A, 1.5 g colloidal sulfur and 3.5 g of maleic anhydride to react at 180° C. for 2 h, yielding a modified asphalt composition, the properties of which are shown in Table 5. It can be seen from Table 3 that the softening point difference determined by the stability test is only 2.5° C.

## Example 9

15 g of SBS was contacted with 2.5 g of naphthenic oil at 25° C. for 48 h, and then to the treated SBS were added 479 g of base asphalt A, 1 g mono-sulfurized alkylphenol (produced by Beijing Chemical Plant) and 2.5 g of polyphosphoric acid produced by Beijing Chemical Plant) to react at 150° C. for 3 h, yielding a modified asphalt composition, the properties of which are shown in Table 5. It can be seen from Table 5 that the softening point difference determined by the stability test is only 2° C.

## Example 10

15 g of SBS was contacted with 30 g of catalytically cracked oil slurry at 100° C. for 7 h, and then to the treated

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SBS were added 450 a of base asphalt B, 2.5 g zinc oxide (produced by Beijing Chemical Plant), and 2.5 g of phenyl formaldehyde (produced by Yanshan Petrochemical Co.) to react at 200° C. for 1 h, yielding a modified asphalt composition, the properties of which are shown in Table 5. It can be seen from Table 5 that the softening point difference determined by the stability test is only 1° C.

## Example 11

75 g of SBS was contacted with 100 g of styrene tar at 150° C. for 2 h, and then to the treated SBS were added 275 g of base asphalt B, 25 g crystallized sulfur (produced by Beijing Chemical Plant) and 25 g of phthalic anhydride (produce by Qingdao Chemical Plant, Shandong) to react at 170° C. for 2.5 h, yielding a modified asphalt composition, the properties of which are shown in Table 5. It can be seen from Table 5 that the softening point difference determined by the stability test is only 1° C.

TABLE 2

Base asphalt	A	B
Penetration (25° C., 100 g, 5 s), dmm	69	90
Softening point (ring-and-ball), ° C.	48	47.5
Ductility (15° C., 5 cm/min), cm	>150	>150
Viscosity (135° C.), centistokes	732	455
Adhesive toughness (25° C.), N.m	4.3	3.2
Saturates, wt %	18.5	7.4
Aromatics, wt %	31.3	51.5
Resin, wt %	35.3	31.8
Asphaltene, wt %	14.9	9.3

TABLE 3

No.	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1
Base asphalt A, wt %	60.0	60.0	94.06	96.04
SBS, wt %	15.0	15.0	2.86	2.86
compatibilizer, wt %	20.0	20.0	0.98	1.0
Cross-linking reagent, wt %	3.0	3.0	0.1	0.1
Organic polar compound, wt %	2.0	2.0	2.0	0
<u>Product properties</u>				
Penetration (25° C.), dmm	50	52	67	65
Softening point (ring-and-ball), ° C.	86.2	88.8	58.5	55.5
Ductility (5° C., 5 cm/min), cm	43	38	35	38
Stability test, ° C.	2.0	2.5	1	45
Viscosity (135° C.), centistokes	2132	2003	980	1002
Adhesive toughness (25° C.), N.m	32.2	28.5	15.3	13.2
Thin film oven (163° C., 5 h)				
Ratio of Penetration, %	92	94	67.5	68.4
Ductility (5° C.), cm	25	24.5	22	28

TABLE 4

No.	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Base asphalt, wt %	A/72.8	A/94.06	B/95.0	B/95.0
SBS, wt %	2.2	2.91	2.9	2.9
compatibilizer, wt %	15.0	0.93	0.5	0.5
Cross-linking reagent, wt %	5.0	0.1	1.0	1.0
Organic polar compound, wt %	5.0	2	0.6	0.6
<u>Product properties</u>				
Penetration (25° C.), dmm	95	83	62	61
Softening point (ring-and-ball), ° C.	58.5	61.5	76.3	78.4
Ductility (5° C., 5 cm/min), cm	86	64	54	48
Stability test, ° C.	0.5	0.5	2.0	1.0

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TABLE 4-continued

No.	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Viscosity (135° C.), centistokes	992	1035	1532	1438
Adhesive toughness (25° C.), N.m	15.2	21.2	35.2	23.3
Thin film oven (163° C., 5 h)				
Ratio of Penetration, %	78.5	82.1	76.1	75.4
Ductility (5° C.), cm	63	53	41	42

TABLE 5

No.	Ex. 8	Ex. 9	Ex. 10	Ex. 11
15 Base asphalt, wt %	A/77	A/95.8	B/90	D/55
SBS, wt %	7	3	3	15
compatibilizer, wt %	15	0.5	6	20
Cross-linking reagent, wt %	0.3	0.2	0.5	5
Organic polar compound, wt %	0.7	0.5	0.5	5
<u>Product properties</u>				
20 Penetration (25° C.), dmm	45	60	85	75
Softening point (ring-and-ball), ° C.	92	58.5	56	74.3
Ductility (5° C., 5 cm/min), cm	65	42	53	54
Stability test, ° C.	2.5	2.0	1.0	1.0
25 Viscosity (135° C.), centistokes	1895	975	876	2658
Adhesive toughness (25° C.), N.m	31.2	16.8	14.2	33.5
Thin Film Oven (163° C., 5 h)				
Ratio of Penetration, %	95.3	76.5	68.5	86.8
Ductility (5° C.), cm	46	31	30	35

30 What is claimed is:  
1. A storage-stable modified asphalt composition, which comprises:

base asphalt 50-97.7 parts by weight;  
polymer having double bonds 2.0-20.0 parts by weight;  
compatibilizer 0.1-20.0 parts by weight;  
cross-linking reagent 0.1-10.0 parts by weight, wherein said cross-linking reagent is one selected from the group consisting of crystallized sulfurs, activated sulfurs, sulfur-donors, "symbolizing" sulfur-donating cross-linking reagents, and a mixture thereof,  
organic polar compound 0.1-10.0 parts by weight,  
and the softening point difference of its product determined by the stability test is lower than 2.5° C.

2. The modified asphalt composition according to claim 1, wherein said base asphalt is one selected from the group consisting of petroleum asphalts, coal-tar asphalts, tar sand asphalts, and native asphalts, or a mixture thereof, wherein the petroleum asphalt is one selected from the group consisting of straight-run asphalts, asphalts obtained by solvent deasphalting, oxidized asphalts, blended asphalts, and a mixture thereof.

3. The modified asphalt composition according to claim 1, wherein said polymer having double bonds is a block polymer of styrene and butadiene in a ratio of 20-45:80-55.

4. The modified asphalt composition according to claim 1, wherein said compatibilizer is one selected from the group consisting of styrene tar, tall oil, acid-containing tall oil, catalytically cracked oil slurry, heavy deasphalted oil, extracted oil obtained by solvent refining, naphthenic acid, naphthenic oil, white oil, coal tar fractions, and a mixture thereof.

5. The modified asphalt composition according to claim 1, wherein said activated sulfur is a sulfur powder, a colloidal sulfur, or a mixture thereof, and said colloidal sulfur is a colloid with an average diameter of 1-5  $\mu$ m prepared by mixing sulfur powder or precipitated sulfur with a dispersion reagent and then grinding.

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6. The modified asphalt composition according to claim 1, wherein said sulfur donor is one selected from the group consisting of sulfur-containing morpholinium compounds, thiuram compounds, polysulfides, and a mixture thereof.

7. The modified asphalt composition according to claim 1, wherein said "symbolizing" sulfur-donating cross-linking reagent is a divalent metal oxide cross-linking reagent.

8. The modified asphalt composition according to claim 1, wherein said organic polar compound is one selected from the group consisting of amine, acid, phenolic resin, aldehyde compounds, and a mixture thereof.

9. The modified asphalt composition according to claim 8, wherein said amine compound is one selected from polyacene polyamine compounds, wherein the polyacene comprises di-, tri- and tetraethylene; and the polyamine comprises hexamethylene diamine, tetramine, penta-amine, or a mixture thereof.

10. The modified asphalt composition according to claim 8, wherein said acid compound is one selected from the group consisting of carboxylic acid, acid anhydride, sulfonic acid, boric acid, phosphoric acid compounds, and a mixture thereof.

11. The modified asphalt composition according to claim 10, wherein said phosphoric acid compound is one selected from the group consisting of polyphosphoric acid, phosphorous acid, modified phosphoric acid, phosphate compounds, and a mixture thereof.

12. The modified asphalt composition according to claim 8, wherein said phenolic resin compound is one selected from the group consisting of formaldehyde alkylphenol resin compounds, wherein the alkyl is p-tert-butyl or p-tert-octyl paraffinic group.

13. The modified asphalt composition according to claim 12, wherein said alkyl is the polar hetero-atom containing alkyl, and said formaldehyde alkylphenol resin comprises formaldehyde phenol resin having sulfur or oxygen atom containing alkyl.

14. The modified asphalt composition according to claim 8, wherein said aldehyde compound is one selected from the group consisting of glycidic aldehyde, formaldehyde, binary aldehydes, furfural, and a mixture thereof, wherein the binary aldehydes are p-phthalic aldehyde or m-phthalic aldehyde.

15. A process for preparing the storage-stable modified asphalt composition according to claim 1, which comprises mixing 50-97.7 parts by weight of a base asphalt, 2.0-20.0 parts by weight of a polymer having double bonds, 0.1-10.0 parts by weight of a compatibilizer, 0.1-10.0 parts by weight of a cross-linking reagent, and 0.1-10.0 parts by weight of an organic polar compound at 100 to 250° C. to react for 5 to 300 minutes, wherein said cross-linking reagent is one selected from the group consisting of crystallized sulfurs, activated sulfurs, sulfur-donors, "symbolizing" sulfur-donating cross-linking reagents, and a mixture thereof.

16. The process according to claim 15, wherein said compatibilizer can be first mixed with the base asphalt, or with the polymer having double bonds, or with the mixture of the polymer having double bonds and the base asphalt; or said compatibilizer can be added at last, and said compatibilizer can be added either once or twice.

17. The process according to claim 15, wherein said base asphalt can be added either once or twice.

18. The process according to claim 15, wherein said process comprises the following steps:

(1) contacting the base asphalt with the compatibilizer at 100° C.-250° C. for 0.1-6 h to yield the treated base asphalt;

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(2) mixing the treated base asphalt with the polymer having double bonds for 0.1-10 h to yield the asphalt mother liquor;

(3) adding the cross-linking reagent, organic polar compound, and optional base asphalt to the asphalt mother liquor at 100° C.-250° C. to react for 5-300 min, yielding the modified asphalt composition; wherein the weight ratio of the base asphalt in step (3) to that in step (1) is 0-50:100-50.

19. The process according to claim 15, wherein said process comprises the following steps:

(1) contacting the base asphalt with the compatibilizer at 100° C.-250° C. for 0.1-6 h to yield the treated base asphalt;

(2) mixing the treated base asphalt with the polymer having double bonds for 0.1-10 h to yield the asphalt mother liquor, (3) adding the cross-linking reagent, organic polar compound, and optional compatibilizer to the asphalt mother liquor at 100° C.-250° C. to react for 5-300 min, yielding the modified asphalt composition;

wherein the weight ratio of the compatibilizer in step (3) to that in step (1) is 0-50:100-50.

20. The process according to claim 15, wherein said process comprises the following steps:

(1) mixing the base asphalt at 100° C.-250° C. with the polymer having double bonds for 0.1-10 h to yield the asphalt mother liquor;

(2) contacting the asphalt mother liquor at 100-250° C. with the compatibilizer at 100-250° C. for 0.1-6 h to yield the treated asphalt mother liquor;

(3) adding the cross-linking reagent, organic polar compound, and the optional base asphalt to the treated asphalt mother liquor to react for 5-300 min, yielding the modified asphalt composition;

wherein the weight ratio of the base asphalt in step (3) to that in step (1) is 0-50:100-50.

21. The process according to claim 15, wherein said process comprises the following steps:

(1) contacting 2.0-20.0 parts by weight of a polymer having double bonds with 0.1-20.0 parts by weight of a compatibilizer at 10° C.-250° C. for 0.1-72 h to yield the treated polymer having double bonds;

(2) heating 50-97.7 parts by weight of the base asphalt to 100° C.-250° C.;

(3) mixing the treated polymer having double bonds with the heated asphalt for 0.1-6.0 h to yield an asphalt mother liquor, and maintaining the temperature of the asphalt mother liquor at 100° C.-250° C.;

(4) adding 0.1-10.0 parts by weight of the cross-linking reagent and 0.1-10.0 parts by weight of the organic polar compound into the asphalt mother liquor to react for 5-300 min, yielding the modified asphalt composition.

22. The process according to any one of claims 15 to 21 wherein said base asphalt is one selected from the group consisting of petroleum asphalts, coal-tar asphalts, tar sand asphalts, and native asphalts, and a mixture thereof, wherein the petroleum asphalt is one selected from the group consisting of straight-run asphalts, asphalts obtained by solvent deasphalting, oxidized asphalts, blended asphalts, and a mixture thereof.

23. The process according to any one of claims 15 to 21, wherein said polymer having double bonds is a block polymer of styrene and butadiene in a ratio of 20-45:80-55.

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24. The process according to any one of claims 15 to 21, wherein said compatibilizer is one selected from the group consisting of styrene tar, tall oil, acid-containing tall oil, catalytically cracked oil slurry, heavy deasphalted oil, extracted oil obtained by solvent refining, naphthenic acid, naphthenic oil, white oil, coal tar fractions and a mixture thereof.

25. The process according to claim 15, wherein said activated sulfur is a sulfur powder, a colloidal sulfur, or a mixture thereof, and said colloidal sulfur is a colloid with an average diameter of 1-5  $\mu$ m prepared by mixing sulfur powder or precipitated sulfur with a dispersion reagent and then grinding.

26. The process according to claim 25, wherein said sulfur donor is one selected from the group consisting of sulfur-containing morpholinium compounds, thiuram compounds, polysulfides and a mixture thereof.

27. The process according to claim 15, wherein said "symbolizing" sulfur-donating cross-linking reagent is a divalent metal oxide cross-linking reagent.

28. The process according to any one of claims 15 and 18 to 21, wherein said organic polar compound is one selected from the group consisting of amine, acid, phenolic resin, aldehyde compounds, and a mixture thereof.

29. The process according to claim 28, wherein said amine compound is one selected from polyacene polyamine compounds, wherein the polyacene comprises di-, tri- and

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tetraethylene; and the polyamine comprises hexamethylene diamine, tetramine, penta-amine, or a mixture thereof.

30. The process according to claim 28, wherein said acid compound is one selected from the group consisting of carboxylic acid, acid anhydride, sulfonic acid, boric acid, phosphoric acid compounds, and a mixture thereof.

31. The process according to claim 30, wherein said phosphoric acid compound is one selected from the group consisting of polyphosphoric acid, phosphorous acid, modified phosphoric acid, phosphate compounds, and a mixture thereof.

32. The process according to claim 28, wherein said phenolic resin compound is one selected from formaldehyde alkylphenol resin compounds, wherein the alkyl is p-tert-butyl or p-tert-octyl paraffinic group.

33. The process according to claim 32, wherein said alkyl is the polar hetero-atom containing alkyl, and said formaldehyde alkylphenol resin comprises formaldehyde phenol resin having sulfur or oxygen atom containing alkyl.

34. The process according to claim 28, wherein said aldehyde compound is one selected from the group consisting of glycidic aldehyde, formaldehyde, binary aldehydes, furfural, and a mixture thereof, wherein the binary aldehydes are p-phthalic aldehyde or m-phthalic aldehyde.

\* \* \* \* \*

**Appendix C**  
***Related Proceedings***

Not Applicable

**TOTAL PETROCHEMICALS**

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In re Application of: Jim Butler et al.

Serial No.: 10/749,259

Confirmation No.: 8566

Filed: December 31, 2003

For: USING EXCESS LEVELS OF  
METAL SALTS TO IMPROVE  
PROPERTIES WHEN  
INCORPORATING POLYMERS  
IN ASPHALT

§ Examiner: Peter Mulcahy

§ Group Art Unit: 1713

§ Attorney Docket No. COS-890

See attached:

1. Transmittal Letter; and
2. First Supplement to Appeal Brief.

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In re Application of:**  
**Jim Butler et al.**  
**Serial No.: 10/749,259**

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**For: USING EXCESS LEVELS OF  
METAL SALTS TO IMPROVE  
PROPERTIES WHEN  
INCORPORATING POLYMERS IN  
ASPHALT**

8 Examiner: Peter Mulcahy

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**Dear Honorable Commissioner:**

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I hereby certify that this correspondence is being facsimile transmitted to the Patent and Trademark Office to the designated fax 571-273-8300, to the attention: Mail Stop AF, Commissioner for Patents, on the date below.

**March 13, 2007**

Date \_\_\_\_\_

Signature - Elaine Barriot

## TRANSMITTAL LETTER

In connection with the above-identified application, Applicants respectfully submit  
First Supplement to Appeal Brief.

The Commissioner is hereby authorized to charge any additional fees that may be required for this submission, or to credit any overpayments to Deposit Account No. 03-3345.

Respectfully submitted,

**Dated**

March 13, 2007

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